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The objectives of this project are to elucidate the chemical and biological mechanisms that control the precipitation and dissolution of arsenic and mercury in anaerobic coastal sediments and to quantify the consequences of these processes in determining the potential release of these toxic elements to the water column and their accumulation in marine organisms.

Based on the preliminary research described in the proposal, rapid progress has been made on both the arsenic and the mercury aspects of this project. In particular, the conditions for the microbial reduction of arsenate to arsenite and the precipitation of arsenite as the arsenic trisulfide solid have been documented. These two processes (reduction of arsenate and precipitation of arsenite) largely determine the environmental mobility of arsenic in anaerobic sediments. The rate of dissolution of mercuric sulfide under various conditions and the rates of oxidation and reduction of dissolved mercury are also being quantified. In addition, according to preliminary data, it appears that, as hypothesized in the proposal, the presence of polysulfides can enhance many fold the rate of microbial methylation of mercury in anaerobic sediments.

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The Chemistry and Transformations of Mercury and Arsenic in Anaerobic Sediments

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ONR Grant #: N00014-96-1-0036

First Year Report

The objectives of this project are to elucidate the chemical and biological mechanisms that control the precipitation and dissolution of arsenic and mercury in anaerobic coastal sediments and to quantify the consequences of these processes in determining the potential release of these toxic elements to the water column and their accumulation in marine organisms.

Building on the preliminary research described in the proposal to ONR, we have been able to make rapid progress on both the arsenic and the mercury aspects of this project. In particular we have documented the microbial reduction of arsenate to arsenite and studied the conditions for precipitation of arsenite as the arsenic trisulfide solid. These two processes (reduction of arsenate and precipitation of arsenite) largely determine the environmental mobility of arsenic in anaerobic sediments. We have also begun to quantify the rate of dissolution of mercuric sulfide under various conditions and the rates of oxidation and reduction of dissolved mercury. In addition, according to our preliminary data, it appears that, as hypothesized in the proposal, the presence of polysulfides can enhance many fold the rate of microbial methylation of mercury in anaerobic sediments. These achievements are described succinctly below.

Arsenic: Arsenic occurs in the environment principally in two forms, arsenate, As(V), which forms stable precipitates mainly with iron, and arsenite, As(III), which in contrast has been generally considered quite soluble and hence mobile. The chemical and biological transformations between As(V) and As(III) in oxic and anoxic environments are thus of particular interest. Following our previous work with MIT-13 (now *Geospirilum arsenophilus*), we have

now isolated a second strain, OREX-4 (now *Desulfitobacterium orex*) that grows by dissimilatory reduction of As(V), and characterized both organisms in terms of their metabolic capabilities. One organism can reduce N(V) as well as As(V), while the other can grow on N(VI) as well as As(V). While MIT-13 is gram-negative, OREX-4 is gram-positive and, according to 16S ribosomal RNA sequencing, the two organisms are phylogenetically quite distant. These results, which are being written-up for publication, demonstrate that As(V) reduction is likely widespread among bacterial phyla and common in contaminated anoxic environs.

In addition to reducing As(V), OREX-4 precipitates As(III) as As_2S_3 in S-containing medium. This precipitation occurs, at least in part, intracellularly and under conditions where no chemical precipitation is observed. This finding puts into question the general assumption that reduction of As(V) to As(III) makes As more mobile in the environment. On the contrary, As_2S_3 precipitation may provide a permanent sink for As in anaerobic sediments. A manuscript on this topic is being submitted to Applied and Environmental Microbiology.

Mercury: The major form of mercury in anoxic sediments is mercuric sulfide (HgS), as cinnabar (red) or metacinnabar (black). These minerals are extremely insoluble and a major question relating to the mobility of Hg in anoxic environments is that of the mechanisms and rate of dissolution of HgS. We have begun a systematic study of the kinetics of HgS dissolution examining the effects of such factors as pH, oxygen concentration, light and the presence of organic acids. At present, it is clear that, as we hypothesized, visible light greatly enchances the kinetics of dissolution as does oxygen. The dissolution process is complicated by the possible reduction of Hg(II) (by sulfur or organic species) and rapid re-oxidation of Hg(0) (ultimately by O_2). The rapid oxidation of Hg(0) in the presence of oxygen seems to have been ignored in the environmental literature and, in many aquatic systems, this process should effectively decrease the net rate of Hg(0) volatilization into the atmosphere. We are in the process of quantifying the rates of each of these chemical reactions under conditions typical of natural sediments.

In addition to the difficulties posed by facile redox reactions, the chemistry of mercury in sediments is complicated by the multiple forms of inorganic sulfur. In particular we have

hypothesized that Hg(II) complexes with polysulfides, S_n^{2-}, may facilitate the bacterial uptake and hence the methylation of mercury. Indeed we have found that addition of 0.1mM polysulfide increases the solubility of HgS about 10 fold at pH's 8-10. Further, in preliminary experiments, the same addition of polysulfides to cultures of methylating bacteria grown under fermentating conditions in the presence of HgS increases many fold the rate of Hg methylation. If these results are confirmed, they will constitute a breakthrough in our understanding of the mechanisms of Hg methylation in anaerobic sediments and of the factors that control it.